



Short communication

Use of non-conventional electrolyte salt and additives in high-voltage graphite/LiNi_{0.4}Mn_{1.6}O₄ batteriesC. Arbizzani^a, F. De Giorgio^a, L. Porcarelli^a, M. Mastragostino^{a,*}, V. Khomenko^b, V. Barsukov^b, D. Bresser^c, S. Passerini^c^aAlma Mater Studiorum Università di Bologna, Department of Chemistry “G. Ciamician”, Via F. Selmi 2, 40126 Bologna, Italy^bKiev National University of Technologies and Design, Nemirovich-Danchenko str.2, 01011 Kiev, Ukraine^cInstitute of Physical Chemistry and MEET Battery Research Centre, University of Muenster, Correns str. 28/30 & 46, 48149 Muenster, Germany

H I G H L I G H T S

- Performance data of high-voltage graphite/LiNi_{0.4}Mn_{1.6}O₄ full cells are shown.
- Beneficial impact of LiFAP with respect to LiPF₆ in EC-DMC for high-voltage batteries is evidenced.
- Effect of F₁EC and SA additives to LF30 on cyclability and self-discharge of full cells is reported.

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The performance of full cells featuring high-voltage LiNi_{0.4}Mn_{1.6}O₄ cathode and graphite anode with carbonate-based electrolytes, ethylene carbonate (EC)–dimethyl carbonate (DMC) with conventional LiPF₆ and non-conventional Li[(C₂F₅)₃PF₃] (LiFAP) lithium salts with and without SEI-forming additives 1-fluoro ethylene carbonate (F₁EC) and succinic anhydride (SA) is investigated. The results evidence the beneficial impact of EC-DMC-1M LiFAP electrolyte (LF30), with respect to EC-DMC-1M LiPF₆ electrolyte (LP30), also in presence of 1.6% F₁EC-2% SA additives, on charge retention over cycling and on self-discharge of full cells. After the 25 cycles of the charge capability test, the charge retention reached values up to 70% with LF30 and 87% with LF30 and additives, and fully charged cells with LF30-additives delivered 53% of the stored charge after one week in OCV.

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1. Introduction

Lithium-ion batteries, which have played a fundamental role in the extraordinary expansion of the electronic market, are still under intensive study for applications in sustainable transportation where high energy and power battery packs are requested to extend electric power-train in full and plug-in hybrid electric vehicles [1,2]. To enhance the specific energy at cell level over 200 Wh kg^{−1} high-voltage cathode materials based on nickel manganese spinel oxides such as LiNi_{0.5−y}Mn_{1.5+y}O₄ ($y \leq 0.1$) with theoretical capacity of 147 mAh g^{−1} are, in the short-term, the most promising candidates in combination with graphite anodes. Among

these spinels, LiNi_{0.4}Mn_{1.6}O₄ has been identified as the best performing, a good compromise between the increase of cycle life and the decrease of the average potential with the introduction in the spinel structure of a small amount of Mn³⁺ which oxidizes to Mn⁴⁺ at 4 V whereas the oxidation of nickel (II) to nickel (IV) occurs at 4.7–4.75 V vs. Li [3]. The potential of Li insertion/extraction in these materials is remarkably high so that the nature of electrolytic medium is of great importance for cell cycling stability and self-discharge [4–7].

The aim of this work is to investigate self-discharge and cycling performance of full cells with LiNi_{0.4}Mn_{1.6}O₄ positive and graphite negative electrodes and carbonate-based (ethylene carbonate and dimethyl carbonate) electrolytes having conventional (LiPF₆) and non-conventional (Li[(C₂F₅)₃PF₃]) lithium salts with and without SEI-forming additives 1-fluoro ethylene carbonate (F₁EC) and succinic anhydride (SA), and to find out by the aid of X-ray

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photoelectron spectroscopy measurements a relationship between the used electrolytes and the cathode interphase properties and cell performance.

2. Experimental

Half and full cells having positive electrodes based on home-made $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ (LNMO) by CEA (Grenoble) and Li in excess and graphite-based negative electrodes, respectively, were assembled. Composition (in wt%) of the positive electrodes was 85% (LNMO), 10% carbon black carbon conducting additive and 5% polyvinylidene fluoride (pVDF) binder and that of the graphite electrodes was 89% graphite (SLA-1025, Superior Graphite), 3% carbon black additive and 8% pVDF. The cathode and anode (active materials) loadings were 7.5 and 2.5 mg cm^{-2} (low mass loading), 14.8 and 5.2 mg cm^{-2} (high mass loading), respectively. Unlike low mass loading cathodes (pressed at 1500 psi) all the electrodes were roll pressed and disk electrodes (0.64 cm^2 and 1.13 cm^2) were dried at 120 °C for 12 h under vacuum before use. The electrode mass balancing in the full cells was made by setting the ratio of the capacity of the negative to that of the positive near 1. Cell assembly was performed in a MBraun Labmaster SP glove box (water and oxygen content < 0.1 ppm), using Whatman GF/D separators in half cells and Celgard 2400 in full cells and solutions of ethylene carbonate (EC):dimethyl carbonate (DMC) 1:1–1 M LiPF_6 (LP30, Merck, water ≤ 20 ppm and HF content ≤ 50 ppm) or EC:DMC–1 M lithium tris(pentafluoroethyl)trifluorophosphate (LF30, Merck, water ≤ 20 ppm and HF content ≤ 50 ppm) with and without additives. The additives were 1-fluoro ethylene carbonate (F_1EC , Solvay Fluor, purity ≥ 99.9 wt%, water and HF content ≤ 20 ppm) and succinic anhydride (SA, Sigma–Aldrich, purity $\geq 99\%$), used as received, and their amount in the electrolyte solutions was 1.6 wt% and 2 wt%, respectively. The electrochemical tests on half and full cells were performed utilizing Swagelok™-type cells in three-electrode configuration with Li as reference electrode at 30 °C, as well as the linear sweep voltammetries (LSVs) on LP30 and LF30 without and with additives at Pt (0.13 cm^2) electrode; in LSVs a Li counter electrode was used. The tests were carried out by a Biologic VMP multichannel potentiostat/galvanostat and by a Maccor Series 4000 Laboratory Testing System and the temperature was controlled by a Memmert IPP 200 Incubator.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with Axis Ultra HSA, Kratos using a monochromatic Al $K\alpha$ source, at 10 mA and 12 kV source energies. To compensate charging of the sample, the charge neutralizer was used. Calibration of the binding energy (BE) of the measured spectra was performed by usage of the energy of the C1s graphite peak (CC at BE = 284 eV) as an internal reference. XPS measurements were performed on pristine cathodes as well as after 30 charge/discharge cycles; hence, cells were disassembled in an argon-filled dry-box and electrodes were analyzed without rinsing to prevent inequality. The samples were transferred to the spectrometer using sealed vials in order to avoid air/moisture contamination. Residual electrolyte was removed by applying ultra-high vacuum overnight before XPS characterization.

3. Results and discussion

Fig. 1 shows the voltage profile of LNMO in a half cell vs. Li during the 1st galvanostatic charge/discharge cycle at C/10 (135 $\mu\text{A cm}^{-2}$) in LP30 between 3.5 V and 4.95 V. The profile clearly displays the redox process near 4 V due to the $\text{Mn}^{3+}/\text{Mn}^{4+}$, which is responsible of one fifth of the total capacity, and the high-voltage processes at ca. 4.7–4.75 V due to $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ couples. The charge/discharge coulombic efficiency is 94% at the first

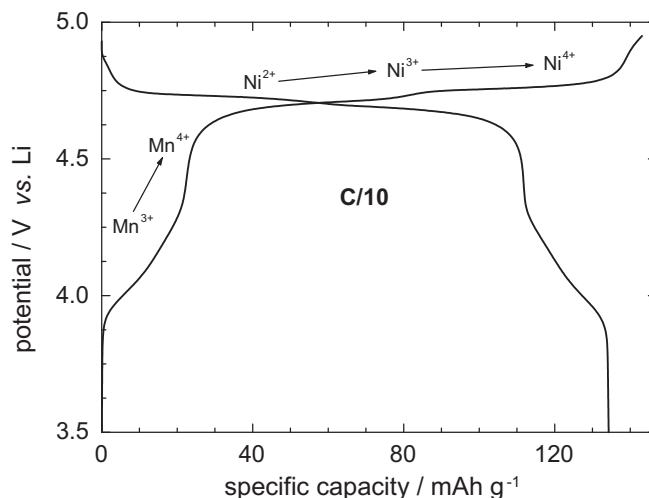


Fig. 1. Voltage profile of LNMO (half cell vs. Li with LP30) over the first cycle at C/10.

cycle and increases to 97% at the third cycle at C/10, a good result despite the thermodynamic instability of the LP30 above 4.5 V. However, self-discharge of the fully charged graphite/LNMO cell with LP30 electrolyte is very high: a cell charged up to 4.95 V lost ca. 50% of the charge after 40 h in open circuit conditions. Furthermore, the results of charge capability tests at 30 °C on low mass loading graphite/LNMO full cells, reported in Fig. 2 (triangles), evidence the low cell performance in LP30. These tests involved galvanostatic cycles at different C-rates from C/10 to 2C during charge and the same discharge rate (C/10) after 30 min in open circuit condition (4 cycles at each C-rate). Additional 4 charge–discharge cycles at C/10 were carried out at the end of the charge capability test for the evaluation of the capacity retention (the ratio between the discharge capacity of the last C/10 cycle and that of the 1st one).

SA (2%) was added to LP30 to protect the cathode, as suggested in ref. [8], as well as F_1EC 1.6% as SEI forming for graphite electrode (instead of vinylene carbonate not suitable in combination with high-voltage cathode [9]). Although the beneficial effect of the two additives on the oxidation potentials of LP30 shown in Fig. 3a, where LSVs at Pt electrode in LP30 with and without additives are compared, the charge capability of the full cell was not sufficiently improved by the addition of the two additives to LP30 as shown in

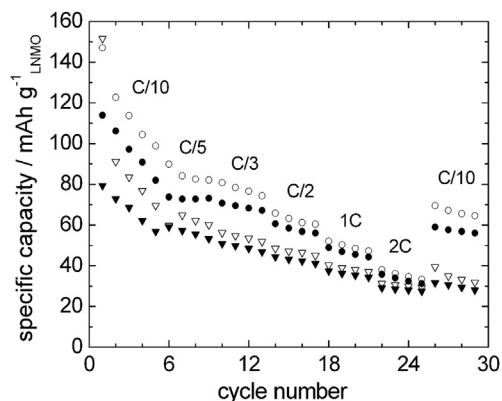


Fig. 2. Specific capacity (referred to the active mass of the cathode) of charge (void symbol) and discharge (full symbol) under charge capability tests at 30 °C of graphite/LNMO full cells having low mass loading electrodes (see Section 2) with LP30 (triangles) and LP30–1.6% F_1EC –2% SA (circles).

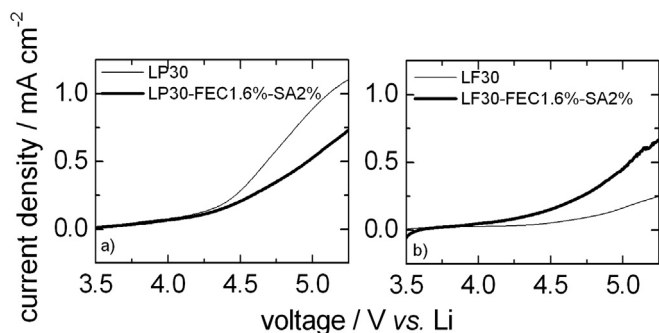


Fig. 3. LSVs at 20 mV s⁻¹ on Pt electrode of (a) LP30 and LP30-1.6% F₁EC-2% SA, (b) LF30 and LF30-1.6% F₁EC-2% SA.

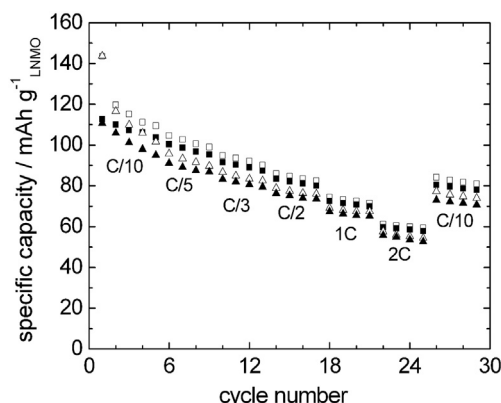


Fig. 4. Specific capacity (referred to the active mass of the cathode) of charge (void symbol) and discharge (full symbol) under charge capability tests at 30 °C of graphite/LNMO full cells having low mass loading electrodes (see Section 2) with LF30 (triangles) and LF30-1.6% F₁EC-2% SA (squares).

Fig. 2 (circles). Even the self-discharge of the fully charged cells was not mitigated by the presence of the additives.

Graphite/LNMO cells with LF30, a commercial electrolyte in which lithium tris(pentafluoroethyl)trifluorophosphate (LiFAP) substitutes LiPF₆, were assembled and tested. LiFAP is less prone than LiPF₆ to hydrolysis and slightly more stable toward oxidation, which is particularly important for high-voltage cathode materials. Moreover, LF30 displays roughly the same conductivity as LP30, and LiFAP has a positive effect on the flashpoint of the organic carbonates compared to LiPF₆, thus improving the safety of the resulting lithium-ion cells [10,11]. Full cells with the two additives to LF30 were also assembled and tested, despite the LSVs at Pt

electrode (Fig. 3b) did not evidence any improvement. Fig. 4 compares the results of charge capability tests performed at 30 °C on low mass loading graphite/LNMO full cells in LF30 (triangles) and in LF30-1.6% F₁EC-2% SA (squares). The recovered charge was ca. 80% at the first cycle (C/10) for both the cells and increased over cycling up to 96% at C/10 and 98% at 1 C. The capacity retention was 64% for the cell in LF30 and 69% for that in LF30 with additives, indicating a slightly positive effect of the two additives.

The comparison of the charge capability data of Figs. 2 and 4 clearly shows the beneficial impact of LF30 with respect to LP30. However, a loss of capacity over the first cycles at C/10, even if much more limited than that of full cells in LP30 with and without additives, still occurred. This phenomenon is mitigated in full cells with high mass loading electrodes as shown in Table 1 which displays the discharge capacity and the corresponding percentage of recovered charge of selected cycles at C/10 at the beginning and at the end of the charge capability tests of full cells with thin and thick electrodes. High loadings, indeed, involve high current densities which are beneficial to limit the contribution of side reactions, particularly in the first cycles where the effect of additives on the recovered charge is more evident, and to increase the capacity retention up to 70% in LF30 and 87% in LF30 with additives.

The results of self-discharge tests of graphite/LNMO cells in LF30 and in LF30-1.6% F₁EC-2% SA are compared in Fig. 5a which displays the discharge voltage profiles at C/10 and the recovered charge of fully charged cells at C/10 at different OCV times (0.5, 20 and 40 h), after five initial cycles (C/10 charge -0.5 h OCV-C/10 discharge). While the cell with LF30 after 20 and 40 h recovered 81% and 73% of the charge, respectively, the cell with LF30 and additives after 20 and 40 h recovered 83 and 75%, respectively. We further investigated the self-discharge in LF30 and additives over longer time and the results of Fig. 5b shows that the cell recovered 72% and 53%, after 72 and 165 h, respectively.

To evaluate the effect of F₁EC and SA on the cathode material XPS measurements were performed on low mass loading cathode, both as made (pristine) and after electrochemical tests in half cells vs. Li, with different electrolytes. The electrochemical tests consisted of 3 charge/discharge cycles at C/10 followed by 27 cycles at C/5 between 4.95 and 3.50 V vs. Li. Fig. 6 shows the spectra of Mn 2p and O 1s. The former, split in two parts because of spin-orbit coupling, displays the Mn 2p_{1/2} peak at ~654 eV and the Mn 2p_{3/2} peak at ~642 eV (intensity ratio of 1:2) for the pristine cathode and the cathode after electrochemical tests in LF30, LF30 and additives and LP30 and additives. After cycling the intensity of the signals is lower due to the deposition of decomposition products of the electrolyte oxidation on the electrode surface. The atomic percentage of Mn for the pristine LNMO and for LNMO that worked in LF30 and LF30-1.6% FEC-2% SA and LP30-1.6% FEC-2% SA was 1.60, 0.59, 0.76, 0.56 respectively. Since the higher is the intensity of

Table 1

Discharge capacity and corresponding percentage of recovered charge of selected cycles at C/10 at the beginning and at the end of the charge capability tests of full cells with thin and thick electrodes and with different electrolytes.

Cycle	LF30				LF30-1.6% F ₁ EC-2% SA			
	Thin		Thick		Thin		Thick	
	Discharge capacity (mAh g ⁻¹ LNMO)	Recovered charge (%)	Discharge capacity (mAh g ⁻¹ LNMO)	Recovered charge (%)	Discharge capacity (mAh g ⁻¹ LNMO)	Recovered charge (%)	Discharge capacity (mAh g ⁻¹ LNMO)	Recovered charge (%)
1	111	77	114	81	113	79	112	85
3	101	92	109	93	107	93	108	97
5	95	94	104	95	104	95	111	97
27	72	96	82	96	80	96	100	96
28	72	96	81	96	79	96	99	96
29	71	96	80	96	78	96	97	96

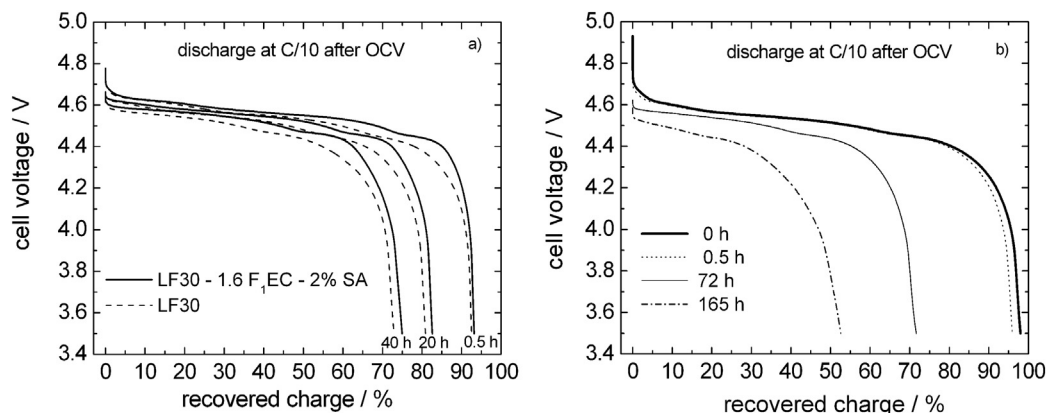


Fig. 5. Recovered charge upon discharge at C/10 of graphite/LNMO full cells, with different electrolytes, charged at C/10 and stored in OCV for different times at 30 °C: (a) LF30 (dash line) and LF30–1.6% F₁EC–2% SA (solid line), (b) LF30–1.6% F₁EC–2% SA.

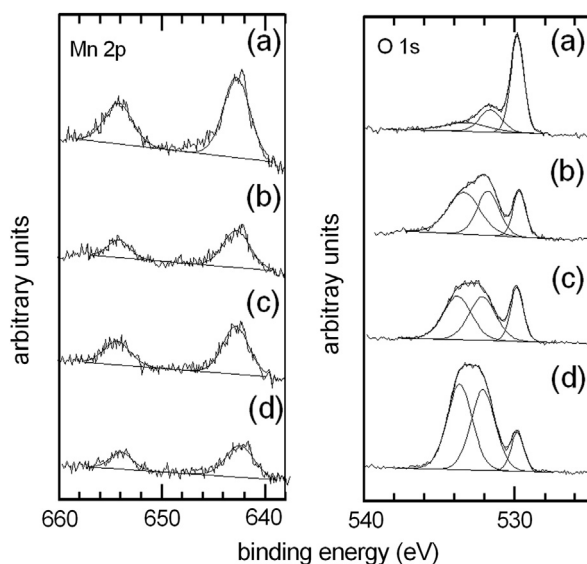


Fig. 6. Mn 2p and O 1s spectra of LNMO electrodes, (a) as-prepared, and cycled 30 times using (b) LF30, (c) LF30–1.6% F₁EC–2% SA, (d) LP30–1.6% F₁EC–2% SA.

the signal of Mn 2p peaks the thinner is the layer coating LNMO, the thinnest layer is formed when LF30–2% SA–1.6% F₁EC is used.

The O 1s spectra of the as-prepared electrode display a narrow peak at –529 eV assigned to the O^{2–} anions of LNMO [12]. After 30 cycles the intensity of the peak lowers and the relative values are in good agreement with those of Mn 2p spectra. The O 1s spectrum of the starting electrode also shows two weak peaks at higher binding energies, respectively at ~530 and ~533 eV, both assigned to absorbed species at the surfaces. The spectra of cycled electrodes display an enhancement of the high binding energy components, which can be attributed to the deposition of oxygenated species as R₂CO₃ and Li₂CO₃ on the surface of the electrode upon cycling. These peaks are much stronger when LP30 with additives is used, thus indicating that the concentration of these species is higher than for the other samples. Hence, the above reported XPS spectra give some indications about thickness and composition of the layer on cathode electrode produced by electrode–electrolyte reactions of the different systems.

4. Conclusion

The results of this study evidence the beneficial impact of EC:DMC–1 M LiFAP electrolyte (LF30), also in presence of 1.6% F₁EC–2% SA additives, with respect to the LP30-based electrolytes on charge retention over cycling and on self-discharge of full cells featuring a graphite anode and an LNMO high-voltage cathode that were completely charged up to 4.95 V. After the 25 cycles of the charge capability test, the charge retention of the cells reached values up to 70% with LF30 and 87% with LF30 and additives, and fully charged cells with LF30–additives delivered 53% of the stored charge after one week in OCV.

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